Short communication

Flexible zinc–carbon batteries with multiwalled carbon nanotube/conductive polymer cathode matrix

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HIGHLIGHTS

- Design and fabrication of flexible zinc–carbon battery.
- MWCNT composite cathode provided superior discharge performance than graphite.
- Functionalization of MWCNTs affected dispersibility and resistance.
- Addition of conductive polymers improved battery performance.

ARTICLE INFO

ABSTRACT

In this paper we demonstrate the implementation of multiwalled carbon nanotubes (MWCNTs) and conductive polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) for the development of highly conductive composite electrode for flexible Zn/MnO_2 batteries. The MWCNTs were found to be more effective than graphite. Though more dispersible, carboxylated MWCNTs appeared to increase the resistance of the electrode and decrease the electrochemical performance. The relatively inexpensive MWCNTs represent an advantage over graphite in flexible composite MnO_2 cathode.

1. Introduction

The increasing interest to flexible/bendable electronics requires the development of flexible energy storage devices which can be implemented in products such as smart cards, memory chips, radio frequency identification tags as well as pharmaceutical and cosmetic transdermal delivery patches. Many of these applications can adopt primary zinc–carbon batteries, with zinc as anode active material and manganese dioxide as cathode active material, implemented in thin, flexible substrates. The production costs of such power sources are relatively low due to water-based electrolyte as well as inexpensive and environmentally friendly electrode materials. Moreover, these flexible batteries can be manufactured by cost-effective printing techniques that are compatible with printable electronics [1,2].

Recent publications [3–5] have focused on the development of different aspects of the flexible zinc–manganese dioxide battery manufacturing processes, including design of the cells, current collectors, electrodes ink as well as electrolyte formulations. The development of highly conductive electrode formulations with minimal amount of inactive components (conductive additive, binder) is particularly important for obtaining higher discharge efficiency.

Due to their high electrical conductivity and large surface area, carbon nanotubes (CNTs) have attracted much attention as effective conductive additives for composite electrodes in electrochemical energy storage devices such as lithium ion batteries and supercapacitors [6–9]. On the other hand, the extraordinary mechanical properties, such as high strength and flexibility, make CNTs a potential key component for engineering of thin and flexible electrodes. The well-formed CNT network in CNT/PANI composite (25% w/w of CNTs) was shown to provide high flexibility to paper-like supercapacitor electrodes [10]. Flexible CNT-$LiMn_2O_4$ cathodes for

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lithium-ion batteries were recently prepared without polymer binder [11]. Carbon nanotubes films (for example, "bucky" paper) have been proposed as lightweight bendable mechanical support/current collector for a composite electrode [12].

Recently, singlewalled carbon nanotubes (SWCNTs) have been utilized as conductive additive for MnO_2-based electrodes in Zn/MnO_2 flexible batteries [13,14]. The efficient conductive network of CNTs resulted in significant enhancement of the discharge capacity compared to conventional carbon black additives [13]. However, SWCNTs are still too expensive to be applied as conductive additives and/or materials for current collectors in commercial batteries.

Since MnO_2 is known to be a poor electrical conductor, a significant amount of conductive additives (usually, graphite or carbon black) are added to the composite cathode in zinc—carbon batteries. There is also the possibility of adding other conducting polymers to enhance conductivity. For example, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), PEDOT is known to be a stable conductive polymer which has been successfully applied as an electrode material for organic solar cells [15], supercapacitors [16,17], and a MWCNT polystyrene composite coated with PEDOT and functionalized insitu with MnO_2 has been used as an electrode in supercapacitors [18].

The objective of this paper is to explore the use of multiwalled carbon nanotubes (MWCNTs) and electroconductive polymer PEDOT:PSS to create highly conductive composite electrodes for flexible zinc—carbon batteries.

2. Experimental

The cathode paste was prepared by mixing MnO_2 powder (Aldrich, $\geq$99.99%, trace metal basis), polyvinylpyrrolidone (PVP, Aldrich, average mol wt. 10,000), 1.3% wt aqueous dispersion of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Aldrich) and MWCNTs (purity 95%, Cheap Tubes Inc. Brattleboro, VT, USA). After mixing the components, the aqueous paste was sonicated for at least 10 min using OMNI SONIC RUPTOR 250 ultrasonic homogenizer. For comparison, the cathode mixture with synthetic graphite (Aldrich, <20 micron) instead of MWCNTs was prepared as well. The MWCNTs used were as received or functionalized prior to the electrode preparation to improve their dispersibility in the solvent/electrode matrix. The functionalization of MWCNTs were performed in a Microwave Accelerated Reaction System (Mode: CEM Mars) using an experimental procedure previously published by our laboratory [19,20]. The typical cathode contained 87.0% w/w MnO_2, 3% w/w PVP, and the rest being MWCNTs and PEDOT:PSS after drying. The MnO_2:MWCNTs ratios in the cathode mixture were varied for formulation optimization.

The anode mixture for flexible batteries was made of zinc powder (Sigma Aldrich, $\leq$10 μm, $\geq$ 98%) mixed with PVP and PEDOT:PSS aqueous solution. Zinc acetate (Sigma Aldrich, $\geq$99.99%) was also added to provide an excess of Zn cations in the mixture and, therefore, to increase the conductivity of the electrode paste [1]. The anode after drying contained 83.5% w/w Zn dust, 2% w/w PVP, rest being PEDOT:PSS and Zn acetate.

The flexible electrodes were prepared by casting the electrode slurry onto the carbon tape (NEM tape, Nisshin EMCO Ltd) current collector. Before casting, the carbon tape was stuck to the adhesive side of polyethylene terephthalate PET film coated with ethylene vinyl acetate copolymer (EVA) resin. The typical electrode area was 4 cm × 5 cm. Copper foil strips stuck to the carbon tape served as electrode tabs. To reduce the resistance, the carbon tape was coated with silver ink before applying electrode mixture (CAIG Laboratories Inc).

After applying the slurry onto the current collector, the electrodes were allowed to dry at ∼50 °C for 30 min. The last 5 min of

Table 1
Surface resistance of MnO2 cathodes with different electrode formulations.

Sample	Surface resistance of 1 cm^2 area (KΩ)	Description of the sample
1	3.26	PVP/MnO_2/raphite
2	0.86	PVP/PEDOT:PSS/MnO_2/Graphite
3	0.37	PVP/PEDOT:PSS/MnO_2/CNTs (raw)
4	0.54	PVP/PEDOT:PSS/MnO_2/CNTs (functionalized)

drying was processed under vacuum (pressure 9.893 kPa, with atmosphere pressure 101 kPa). The drying was complete with no residual water. The typical weights of the cathode and anode after drying were 0.5 and 1 g, respectively. The electrodes were assembled co-facially with the craft paper separator (MUNKSJÖ paper) in between, which had been previously soaked in saturated zinc acetate electrolyte. The electrolyte also contained 600 ppm lead chloride and 1000 ppm hexadecyltrimethylammonium bromide (HDTAB, Sigma Aldrich, $\geq$99%) as inhibitors [1]. The battery was finally thermally sealed.

The electrochemical performance of MnO_2 cathodes was also measured in metal cells with Zn-foil as anode to optimize the formulation. In this case the cathode slurry was cast directly onto the stainless steel current collector (25 mm diameter) and dried. The typical weight of the cathode paste after drying was 0.1 g. For both "rigid" and flexible cells, the Zn anode was taken in excess in respect to MnO_2 cathode.

Scanning electron microscope (SEM) images were collected on a LEO 1530 VP Scanning Electron Microscope. Electrode materials were cast onto flat surface and dried to form a 0.2 mm thick layer of 1 cm × 1 cm. The surface resistance between two ends of the above layer was measured using Keithley digital multimeter to compare the electrode conductivity. The electrochemical performance of the battery was measured by discharging in a constant resistance mode (2640 Ω) using MTI Battery Analyzer (Richmond, CA). Thus discharge current dropped with time. For the electrochemical performance measurement under bending conditions, the battery was firmly attached over a cylindrical solid substrate of different diameters to provide the required curvature.

3. Results and discussion

The surface resistance of the cathode composed of MnO_2, graphite and PVP was 3.26 kΩ (see Table 1). In addition, PEDOT:PSS
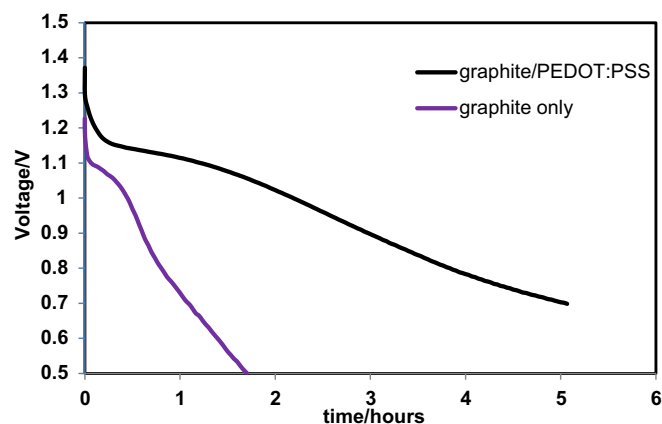

Fig. 1. Discharge curves of cathodes prepared with and without PEDOT:PSS. Graphite (8.6% w/w) was added as the conductive additive. The discharge was performed in constant resistance mode in a metal cell with Zn-foil anode and $Zn(CH_3COO)_2$ electrolyte.
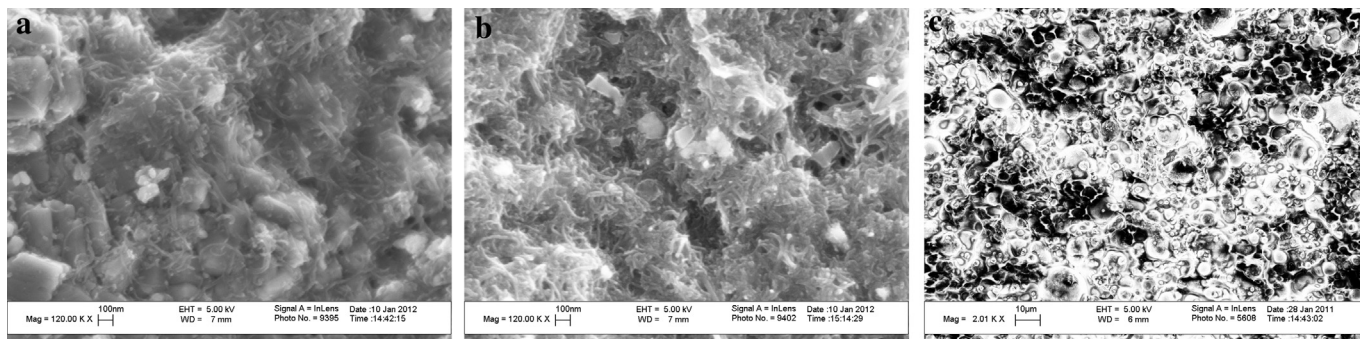
Fig. 2. SEM images of the composite electrodes: a) MnO_2-cathode (8.6% raw MWCNTs as conductive additive), b) MnO_2-cathode (8.6% w/w functionalized MWCNTs as conductive additive), c) anode made of micron size Zn particles.

was added to increase the overall conductivity of the MnO_2 cathode. The addition of 1% PEDOT:PSS significantly reduced the resistance of the cathode down to 0.86 kΩ. The internal resistance of the electrodes may have contributed to lowering the operation voltages compared to the theoretical value. The addition of PEDOT:PSS to our composite electrode (1% w/w) had a strong impact on the electrochemical performance (Fig. 1). Besides being a conductive polymer [21–23], the PEDOT:PSS showed poor solubility in the electrolyte. It is inferred that the PEDOT:PSS formed a conductive layer on the electrode surface during drying and remained stable in presence of the electrolyte after the battery was assembled, thus forming more stable electrodes. PEDOT layer could bridge MWCNT and MnO_2 as it has been reported to do in supercapacitor electrodes [18]. As shown in Fig. 1, when the conductive polymer was added to the cathode together with graphite, the discharge plateau was more pronounced and was located in higher voltage range. Effects of PEDOT on the electrodes were also clearly evident by the significant decrease in electrode resistance fabricated for supercapacitors [18]. In general, the improvement in electrochemical performance upon the addition of the PEDOT:PSS was attributed to the presence of highly conductive and stable binder, which increased the overall conductivity of the cathode. Besides its role as a conductive additive, PEDOT:PSS can also act as a binder and thickener for the electrode slurry together with PVP.

As compared to graphite, the MWCNTs decreased the resistance of the cathode from 0.86 to 0.37 kΩ. This indicated that MWCNTs were more effective in creating the conductive network. The electrode prepared with functionalized MWCNTs demonstrated slightly higher resistance (0.54 kΩ) than the ones with raw MWCNTs. The hydrophilic carboxylation usually leads to improved
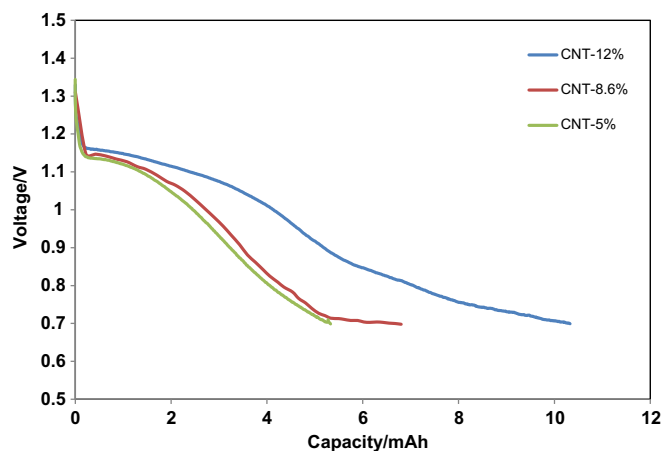

Fig. 4. Voltage–capacity curves for Zn/MnO_2 cells with different concentrations of raw CNTs in the cathode. The discharge was performed in constant resistance mode in a metal cell with Zn-foil anode and $Zn(CH_3COO)_2$ electrolyte.

wettability and dispersibility [24]. Therefore, carboxylation may significantly enhance the electrical conductivity of CNT composites by promoting better interfacial interactions [25–27]. On the other hand, the covalent functionalization can create large number of defects on the surface of CNTs and decrease electron mobility and conductivity. In this case, it appears that the improvement in dispersibility did not outweigh the increase in resistivity. The SEM images confirmed this assumption (Fig. 2a,b) where relatively homogeneous distribution of both raw and functionalized MWCNTs was observed in the composite cathodes. No significant enhancement of the homogeneity was observed after carboxylation of
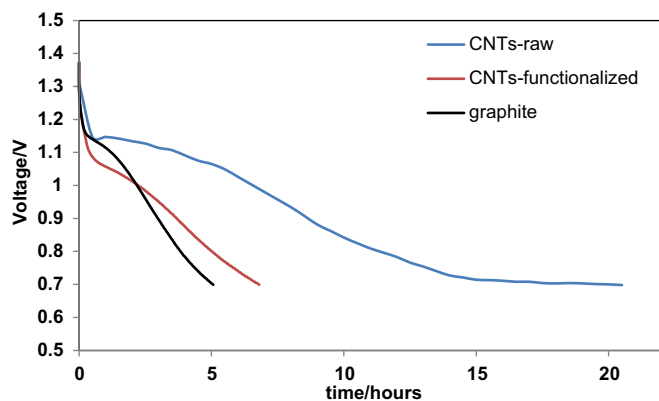
Table 2
Specific performance data of different cells (in metal cells).

Description of the cell	Specific capacity (mAh g^{-1} MnO_2)	Specific energy (mWh g^{-1} MnO_2)	MnO_2 utilization (%)
MnO_2/Graphite	4.50	4.27	1.5
MnO_2/Graphite/PEDOT:PSS	21.0	20.4	6.82
PVP/PEDOT:PSS/MnO_2/CNTs (8.6%, raw)	77.3	71.0	25.1
PVP/PEDOT:PSS/MnO_2/CNTs (8.6%, functionalized)	27.1	25.4	8.80
PVP/PEDOT:PSS/MnO_2/CNTs (5%, raw)	61.5	58.7	20.0
PVP/PEDOT:PSS/MnO_2/CNTs (12%, raw)	120	111	39.0

Fig. 3. Discharge curves for the electrochemical cells with different carbons (8.6% w/w). The discharges was performed in constant resistance mode in a metal cell with Zn-foil anode and $Zn(CH_3COO)_2$ electrolyte.
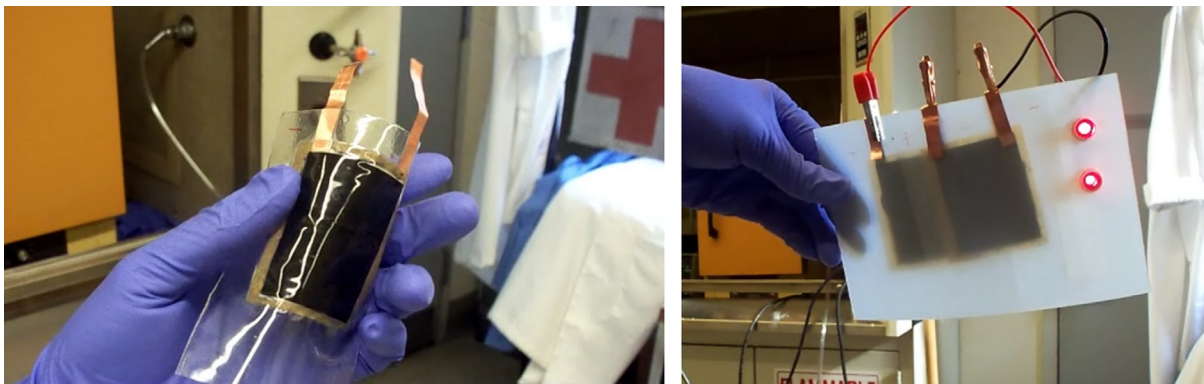
Fig. 5. Photograph of the flexible battery (top) and LEDs powered by the flexible batteries.

MWCNTs. Therefore, in this case, the functionalization did not improve electrode performance.

The electrochemical performance of MnO_2 cathodes prepared with 1% PEDOT:PSS and different carbon conductive additives, namely, graphite, raw MWCNTs and COOH-functionalized MWCNTs (Fig. 3) were measured. Upon discharge down to 0.7 V, the cathode with raw MWCNTs exhibited the highest operation voltage and longest operation time (see Fig. 3). The superior performance of raw MWCNTs compared to the graphite is in good agreement with the results of the resistance measurements. The presence of the conductive additive and the more efficient network of the MWCNTs resulted in higher conductivity and a higher discharge voltage. Increasing the concentration of raw MWCNTs resulted in the higher operation voltage and higher discharge capacity. This is seen from Fig. 4. Performance data of different cells are listed in Table 2, which shows that increasing the concentration of CNTs enhanced battery performance. The specific capacity obtained for the cathode with 8.6% graphite to 12% MWCNTs increased from 4.5 to 120 mAh g^{-1}. The corresponding MnO_2 utilization for the graphite and the MWNT system increased from 1.5 to 39% of the theoretical value of 308 mAh g^{-1} MnO_2. This value is in line with what has been reported before with SWCNTs [14]. It should be noted that a different discharge mode was used in that study [14].

Anode made of micron size zinc powder (Fig. 2c) not only showed higher flexibility than zinc foil, but also had greater surface area facilitating a faster reaction. However, anodes with zinc nanoparticles showed significant corrosion and the batteries failed rather quickly. It is possible that the nanoparticles enhanced the gassing side reaction, generating hydrogen. Consequently, particle size of the zinc powder was an important factor.

The flexible battery prepared with composite cathode and Zn-powder anode is shown in Fig. 5. Upon discharge at a constant resistance of 2640 Ω, the flexible battery delivered about 15 mAh capacity before significant voltage drop occurred. Typically, bending of the flexible battery can induce a compression of the cell stacking enhancing inter-particle contact and can also vary the contact adhesion between the electrodes and the separator. Bending may also result in cracking in some areas due to the stress on the composite especially in the case of MnO_2. These factors are known to cause variation in performance [14]. Testing the batteries under bending conditions revealed that for the most part the batteries retained their function, though there were some relatively small fluctuations and alterations in the performance. This is presented in Fig. 6. In our opinion, the bending performance can be further improved by further optimization of the electrode composition, improving its mechanical properties and packaging process, and by the utilization of more conductive current collectors.

4. Conclusions

We have demonstrated a new approach to the fabrication of MnO_2 composite cathodes based on simultaneous use of conductive polymer PEDOT:PSS and MWCNTs as conductive additives. MWCNTs were found to be more effective in creating conductive networks compared to graphite. The oxidative functionalization of CNTs prior to the cathode fabrication appeared to increase the resistance of the electrode composite and to decrease the electrochemical performance. The relatively inexpensive raw MWCNTs represent an advantageous alternative to significantly more expensive SWCNTs or less effective graphite in composite MnO_2 cathode.

Fig. 6. Voltage–capacity curves for flexible batteries under different bending conditions.

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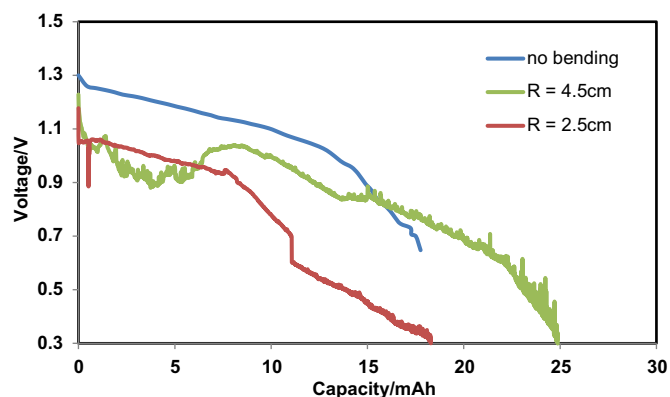[11] X. Jia, C. Yan, Z. Chen, R. Wang, Q. Zhang, L. Guo, F. Wei, Y. Lu, Chem. Commun. 47 (2011) 9669.

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